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(54) Title: ANTIFOULING COATING COMPOSITIONS		
(57) Abstract An antifouling coating composition comprises a water-erodible binder polymer having protected acid functionality and includes an ingredient having biocidal properties for marine fouling organisms. The binder polymer is a star polymer having at least 3 limbs radiating from a central core, the acid functionality being present in the said limbs of the polymer. The protected acid functionality can for example be carboxylic acid functionality protected by a divalent metal or organometallic radical bonded to the residue of a monobasic organic acid, a monoamine or quaternary ammonium groups, triorganosilyl groups or triorganotin groups, or sulphonic acid functionality blocked by a monoamine or quaternary ammonium group.		

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Antifouling Coating Compositions

Field of the invention

This invention is concerned with antifouling coating compositions used on surfaces likely to come into contact
5 with seawater or fresh water containing aquatic fouling organisms such as algae, seaweed and barnacles, for example on ships or boats or fishing nets or on the outfalls for cooling water from power stations. Such coating compositions generally comprise a biocide for marine
10 organisms and a binder polymer. More particularly, the invention relates to antifouling coating compositions having an improved binder polymer.

Background art

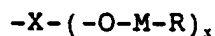
The most successful antifouling paints in recent years
15 have been self-polishing antifouling paints using binders which are substantially linear polymers containing pendent side groups (hereinafter called "leaving groups") which are liberated from the polymer by reaction with seawater, the residual polymer being sufficiently dispersible or soluble
20 in seawater to be swept away from the paint surface, exposing a fresh layer of the binder able to undergo a similar reaction with seawater. Such paints are described for example in GB-A-1,457,590. The gradual thinning of the paint film controls the release of a biocide active against
25 fouling. The well-known benefits of such self-polishing paints are that the paint film tends to at least retain its initial smoothness and that the biocide contained in the paint tends to be delivered from the surface at a more uniform or constant rate.

30 The most commercially significant self-polishing paints employ binders which comprise triorganotin ester leaving groups. The triorganotin provides biocidal activity and the triorganotin ester readily undergoes the hydrolysis on which the self-polishing action is dependent. The biocidal
35 activity can be augmented by one or more other antifouling

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substances dispersed or dissolved in the paint film. There may be advantages in replacing some or all of the triorganotin ester leaving groups by other leaving groups, which are not necessarily biocidal, both for cost reasons 5 and because the powerful biocidal effects of triorganotin may not be desired. There has been concern about the environmental effect of triorganotin biocides released from yachts in particular.

EP-A-204,456 and EP-A-220,965 disclose a hydrolyzable 10 resin composition consisting essentially of a resin having at least one side chain bearing at least one terminal group of the formula:



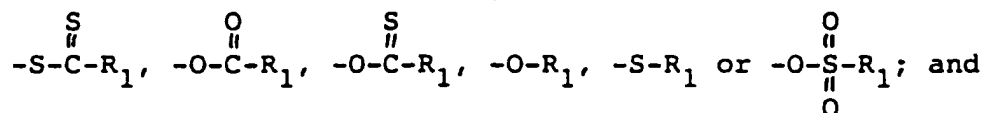
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wherein X represents $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{OH} \end{array}$ or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \end{array}$

M is a metal selected from zinc, copper and tellurium;

x is an integer of 1 to 2;

20 R represents an organic acid residue selected from



R₁ is a monovalent organic residue,

25 and an organic solvent in which said resin is soluble. The hydrolysable resin composition can be used as the binder for an antifouling paint and gradually becomes dissolved in seawater to give controlled release of an antifouling agent.

EP-A-342,276 describes an improved preparation of such a 30 resin composition by reacting a mixture of:-

- (A) acid group-containing base resin,
- (B) metallic salt of low-boiling organic monobasic acid, in which the metal is selected from the members having 2 or more valence and lesser ionisation tendency than 35 those of alkali metals, and

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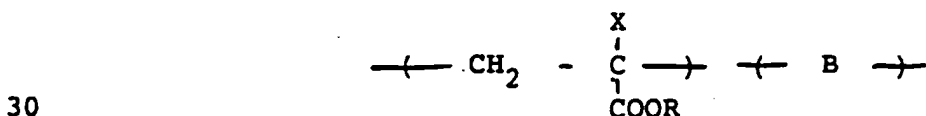
(C) high-boiling organic monobasic acid,
at an elevated temperature while removing the formed low-boiling organic monobasic acid out of the system.

US-A-5,116,407 describes an antifouling coating
5 composition comprising a pigment and as binder a film-forming addition polymer of molecular weight 1,000 to 100,000 containing acid groups, which acid groups are blocked by a hydrolysable blocking group, the composition including an ingredient having marine biocidal properties,
10 said hydrolysable blocking groups being a monoamine group which forms an organic-solvent-soluble amine salt of the film-forming addition polymer.

WO-A-91/09915 describes an antifouling coating composition which comprises a marine biocide and a binder
15 which is a hydrolysable film-forming seawater-erodible polymer, characterised in that the polymer contains sulphonic acid groups in quaternary ammonium salt form.

EP-A-232,006 describes a water-erodible coating comprising at least one erodible polymer comprising one or
20 more hydrolysable groups selected from sulphonate esters and sulphate esters which in an aqueous environment will generate by hydrolysis corresponding polymer-bound acid groups.

WO-A-84/02915 discloses an antifouling paint having a
25 hydrolysable film-forming water-insoluble seawater-erodible polymeric binder having recurring groups represented by the formula



where X is hydrogen or methyl, R is a triorganosilyl moiety or certain substituted alkyl, aryl or aralkyl moieties and B is the residue of an ethylenically unsaturated comonomer.

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Other antifouling coatings based on non-toxic leaving groups bonded by a hydrolysable ester bound to an acid-functional copolymer are described in US-A-4,426,464 and US-A-4,752,629.

5 The use of star polymers in cross-linking coatings is suggested in EP-A-448,224 and in a paper by F. Ciardelli et al, in J. Coatings Technology, Vol.61, No.775, August 1989 at pages 80-85. EP-A-448,224 describes a copolymer having
10 a hub portion from which radiate from 3 to 8 arms, where the hub portion is the residue of a tri-functional to octa-functional thiol and each arm is an addition polymer comprising structural units and functional units that are mutually compatible, the functional units including crosslinking substituents capable of undergoing a
15 crosslinking reaction with a crosslinking agent or the same or a complementary substituent in functional units in another molecule of the same polymer and optionally compatible auxiliary functional units that contain wetting groups. The Ciardelli et al paper refers to star polymers
20 formed using trifunctional (trimethylolpropane trithioglycolate) or tetrafunctional (pentaerythritol tetramercaptopropionate) mercaptans or formed by group transfer polymerisation.

Disclosure of the Invention

25 An antifouling coating composition according to the invention comprises a water-erodible binder polymer having protected acid functionality and includes an ingredient having biocidal properties for aquatic fouling organisms, and it is characterised in that the binder polymer is a
30 polymer having at least 3 limbs radiating from a central core, the acid functionality being present in the said limbs of the polymer. Such a polymer having at least 3 limbs radiating from a central core is referred to hereafter as a star polymer. The binder polymer may itself be the
35 ingredient having aquatic biocidal properties, for example the blocking group protecting the acid functionality may

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have aquatic biocidal properties; alternatively or additionally the composition can contain an added biocide for aquatic organisms.

The use of star polymers in the coating compositions of the invention has several advantages. The viscosity of solutions of the star polymers is less than the viscosity of solutions of the same concentration in the same solvent of a linear polymer of similar molecular weight, so that coating compositions having a higher content of non-volatile solids can be made at a viscosity suitable for conventional application means, for example airless spray. Polishing antifouling paints can be formed from the coating compositions of the invention containing 55% or more by volume of non-volatile material and having a viscosity which makes them suitable for application by conventional airless spray equipment, for example 300-1000 mPa s (3-10 poise). Moreover, coating compositions containing the star polymers have less tendency to increase in viscosity or to gel on storage. This applies particularly to coating compositions containing a copper or zinc compound as antifouling agent. It is believed that the intermolecular crosslinking reactions which cause gelation or increased viscosity are replaced in part by intramolecular crosslinking between acid groups on different limbs of the star polymer, which does not lead to increased viscosity or gelation.

When forming hydrolysable metal-containing resins by processes such as those described in EP-A-204,456 and EP-A-342,276, the star polymer is also less liable to suffer gelation or intermolecular crosslinking during preparation of the metal-containing resin.

The star polymer having protected acid functionality can in general be prepared by one of two procedures. An ethylenically unsaturated monomer having acid functionality and at least one ethylenically unsaturated comonomer can be

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copolymerised by addition polymerisation in the presence of a polyfunctional initiator or chain-transfer agent to form a star polymer having pendent acid functionality, and the star polymer having acid functionality can then be reacted
5 with a reagent introducing blocking groups which protect the acid functionality. The residue of the initiator or chain-transfer agent forms the core of the star polymer. The acid functionality of the monomer is usually free acid functionality, but can alternatively be any acid-functional
10 group which is at least as reactive as the free acid, for example acid chloride or acid anhydride functionality. Alternatively, an ethylenically unsaturated monomer having protected acid functionality and at least one ethylenically unsaturated comonomer can be copolymerised by addition
15 polymerisation in the presence of a polyfunctional initiator or chain-transfer agent to produce a star polymer having protected pendent acid functionality.

The acid functionality can be carboxylic acid functionality, sulphonic acid functionality or phosphonic
20 acid functionality. Examples of monomers having carboxylic acid functionality are acrylic monomers such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, itaconic anhydride or 2-carboxyethyl acrylate or methacrylate, and also vinylbenzoic
25 acid (for example p-vinylbenzoic acid) and 3-butenic acid. Examples of monomers having sulphonic acid functionality are acrylic monomers such as 2-acrylamido-2-methyl-propane-sulphonic acid (AMPS) and 2-sulphoethyl acrylate or methacrylate, and also styrene sulphonic acid (for example
30 p-styrene sulphonic acid), styrene sulphonyl chloride, methallyl sulphonic acid and vinyl sulphonic acid. Examples of monomers having phosphonic acid functionality are 2-acrylamido-2-methyl-propane-phosphonic acid, vinyl phosphonic acid and 2-phosphonoethyl methacrylate.

35 Examples of ethylenically unsaturated comonomers which can be copolymerised by addition polymerisation with such

carboxylic acid, sulphonic acid or phosphonic acid monomers are acrylic or methacrylic esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, butyl acrylate, isobutyl methacrylate, butyl methacrylate or 2-ethylhexyl methacrylate, styrene, acrylonitrile, vinyl acetate, vinyl butyrate, vinyl chloride or vinyl pyridine. Terpolymers may be preferred, for example methyl methacrylate or ethyl methacrylate which tend to form a hard film can be used in conjunction with an acrylate such as ethyl acrylate or particularly an alkyl acrylate of 3 to 8 carbon atoms in the alkyl moiety such as butyl acrylate, which helps to form a more flexible film. A substituted acrylate ester can be used as one of the comonomers, for example methoxyethyl acrylate or methacrylate. When the acid monomer is highly hydrophilic, for example AMPS, it may be preferred to include a hydrophobic comonomer, for example isobornyl methacrylate or a comonomer containing an alkyl chain of at least 6 carbon atoms such as 2-ethylhexyl methacrylate or lauryl methacrylate.

20 A star copolymer having protected carboxylic acid functionality generally contains at least 10 mole % and preferably at least 15 mole % of the monomer units having protected acid functionality, up to 60 mole %, preferably up to 45 mole %. Most preferably, the copolymer contains 15 to 35 mole % of the monomer units having protected carboxylic acid functionality.

A star copolymer having protected sulphonic acid functionality generally contains at least 2 mole % and preferably at least 4 mole % of the monomer units having protected acid functionality, up to 40 mole %, preferably up to 20 mole %. Most preferably, the copolymer contains at least 5 mole % up to 10 or 15 mole % of the monomer units having protected sulphonic acid functionality.

A star copolymer having protected phosphonic acid functionality generally contains at least 3 mole % and

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preferably at least 5 mole % of the monomer units having protected acid functionality, up to 40 mole %, preferably up to 25 mole %. More preferably, the copolymer contains at least 10 mole % up to 15 or 20 mole % of the monomer units 5 having protected phosphonic acid functionality.

The preferred method for generating star polymer architecture is by polymerisation in the presence of a polyfunctional mercaptan, preferably one having 3 or 4 to 8 -SH groups, so that the central core of the star polymer 10 will be the residue of such a mercaptan. Alternative known methods of generating star polymer architecture such as group transfer polymerisation or anionic polymerisation can be used, but they are less convenient for use with acid-functional monomers, particularly acrylic monomers. They 15 can be used to produce 'living' polymers which can be tipped with an acid-functional or protected acid-functional group in a subsequent reaction. A preferred star polymer has 3 to 8 limbs.

Examples of polyfunctional mercaptans are esters of a 20 polyol with a mercapto-substituted acid, preferably a mercapto-substituted aliphatic carboxylic acid. Trimethylolpropane tri(thioglycolate), pentaerythritol tetra (3-mercaptopropionate), trimethylolpropane tri(mercaptopropionate) and pentaerythritol tetra 25 (thioglycolate) are available commercially. Other polyfunctional mercaptans can be formed by reaction of a polyol with thioglycolic acid (mercaptoacetic acid), 3-mercaptopropionic acid or another mercapto-substituted alkanolic acid such as 2-mercaptopropionic acid or 5- 30 mercaptovaleric acid. For example, glycerol or trimethylolethane can be reacted with the mercapto-substituted alkanolic acid, or a more highly functional mercaptan, for example having 5 to 8 mercaptan groups, can be formed by reaction of a more highly functional polyol 35 such as dipentaerythritol or sorbitol, mannitol or a similar sugar alcohol.

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The amount of polyfunctional mercaptan used is generally in the range 0.1 to 4 mole % based on total monomers, usually about 0.3 to 16 mole % thiol groups based on total monomers. The polyfunctional mercaptan acts as a chain transfer agent and hence tends to produce polymers of low molecular weight. For example, the use of 2 mole % pentaerythritol tetra(mercaptopropionate) tends to produce acrylic star polymers having a weight average molecular weight of about 2000 to 3000 for each limb. The theoretical molecular weight for such a polymer is about 10,000, although the molecular weight as measured by gel permeation chromatography (G.P.C.) is about 6,000. The molecular volume of star polymers leads to relatively low measurements using G.P.C. In general, the weight average molecular weight of the star polymer is preferably in the range 3000 to 50,000 measured by G.P.C. against a polystyrene standard, with a weight average molecular weight of each limb of 1000 to 6000. The star polymer preferably has an average functionality of at least one protected acid group per limb of the polymer.

When preparing star polymers using a polyfunctional mercaptan, the monomers, a free radical initiator such as an azo compound, for example azobisisobutyronitrile (AIBN), or a peroxide, for example benzoyl peroxide, and the polyfunctional mercaptan are caused to react together at temperatures conventional for addition polymerisation of acrylic monomers, for example 60 to 140°C. Polymerisation is preferably carried out in an organic solvent, for example an aromatic hydrocarbon, a ketone, ester, alcohol or ether-alcohol such as xylene, toluene, butyl acetate, butanol, methyl isobutyl ketone, butoxyethanol, methoxypropanol or methoxypropyl acetate or a mixture of two or more of these. The monomers, initiator and polyfunctional mercaptan can for example all be added gradually to a reaction vessel containing solvent at the desired polymerisation temperature. The reaction vessel is preferably equipped with cooling means; the mercaptan acts as a catalyst of the

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polymerisation reaction once polymerisation has been initiated. It may also be prudent either to cool the mixture of monomers, initiator and mercaptan, for example at 0 to 10°C, before it is added to the reaction vessel or to
5 add one of these three types of reagent from a separate reservoir from the other two.

The acid functionality of the binder polymer can for example be protected by a divalent metal bonded to the residue of a monobasic organic acid. The acid functionality
10 protected in this way is preferably carboxylic acid functionality, but can alternatively be sulphonic or phosphonic acid functionality. The divalent metal is preferably copper, although other divalent metals such as zinc, manganese, cobalt, nickel or magnesium can be used.
15 A divalent organometallic radical, for example a dialkyl tin radical, can be used in place of the divalent metal. The monobasic organic acid to which the divalent metal or organometallic radical is bonded is preferably a carboxylic acid, but can alternatively be a mono- or di-thiocarboxylic
20 acid or a sulphonic acid.

Such a binder polymer having protected acid functionality is preferably formed by forming a star polymer having acid functionality and reacting this with:-

- (a) a salt of a low-boiling organic monobasic acid and a
25 divalent metal, and
 - (b) a high-boiling organic monobasic acid
- at an elevated temperature while removing from the reaction the low-boiling organic monobasic acid which is evolved, in accordance with the procedure described in EP-A-342,276.
- 30 The star polymer having acid functionality is preferably a copolymer of acrylic or methacrylic acid and one or more alkyl acrylate and/or methacrylate esters polymerised in the presence of a polyfunctional mercaptan. The low-boiling organic acid preferably has a boiling point of below 200°C.
- 35 The salt is for example an acetate or propionate. The high-boiling organic monobasic acid preferably has a boiling

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point (or decomposition temperature) at least 20°C, most preferably at least 50°C, higher than the boiling point of the low-boiling acid. Preferred high-boiling acids are those of the formula $R^1\text{COOH}$ where R^1 is an alkyl, 5 cycloalkyl, substituted alkyl or alkenyl group having at least 6 and most preferably 8 to 18 carbon atoms, for example oleic, stearic, 12-hydroxystearic, lauric, neotridecanoic, neodecanoic, myristic, ricinoleic and linoleic acids and those acids sold commercially as 10 naphthenic acid and versatic acid. Other acids which can be used as the high-boiling acid are, for example, phenoxyacetic, salicylic, p-toluenesulphonic and p-phenylbenzoic acids. The metal salt of the low-boiling organic monobasic acid (a) and the high-boiling organic 15 monobasic acid (b) are each preferably used in a substantially stoichiometric amount based the acid groups of the binder polymer, for example at 0.8 to 1.2 moles per mole of acid groups in the binder polymer. The reaction between the acid-functional star polymer, the polyvalent metal salt 20 and the high-boiling organic acid is preferably carried out at 80-140°C with removal of the evolved low-boiling organic acid by distillation. The reaction can be carried out in the presence of a catalyst, for example 0.03 to 2% by weight of an organotin compound such as dibutyltin dilaurate. The 25 reaction is preferably carried out in solvent, for example an aromatic hydrocarbon such as xylene or trimethylbenzene and/or a ketone or ester solvent having a similar boiling point. Part of the solvent is usually removed from the system by distillation with the low-boiling organic acid as 30 the reaction progresses.

The product of the above reaction is a binder polymer having protected acid functionality; one or more of the acid groups of the binder polymer are converted to groups of the formula $-X-(\text{-O-M-R})_x$ as defined in EP-A-204456, for example

35 to $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{Cu}-\text{O}-\text{C}-\text{R}^1 \\ \parallel \\ \text{O} \end{array}$ groups using copper acetate and a high-

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boiling monobasic carboxylic acid $R'COOH$. There may also be crosslinks formed when a divalent metal atom becomes bonded to two of the groups of the binder polymer, and some metal dicarboxylate may also be formed. This is acceptable provided that the composition does not gel or become too viscous to handle; we have found that the reaction product, provided that it is not crosslinked to the point of gelation, will function effectively as a water-erodible binder for an antifouling coating.

10 Binder polymers containing acid functionality protected by a divalent metal and monobasic organic acid, for example copper carboxylate blocking, can alternatively be prepared from acid-functional star polymers by reactions (2) and (3) described in EP-A-204,456. The acid-functional star
15 polymers can be reacted with an oxide, hydroxide, sulphide or chloride of a divalent metal, for example copper, and a monobasic organic acid, for example an acid of the formula $R'COOH$ as described above, or with a salt of the divalent metal and the monobasic organic acid.

20 In a further alternative, but less preferred, method of preparation of a binder polymer containing acid functionality protected by a divalent metal and monobasic organic acid, for example copper carboxylate blocking, a divalent metal mixed salt with a polymerisable unsaturated
25 organic acid such as acrylic or methacrylic acid and a monobasic organic acid can be prepared as described in EP-A-204,456 as reaction (1). This mixed salt can then be polymerised in the presence of a free radical initiator and a polyfunctional mercaptan.

30 In any of the above reactions, there is a risk that the divalent metal will form a bond between two acid groups each of which are pendent from a polymer chain. When such a bond is formed between two acid groups pendent from different polymer molecules, the resulting crosslinking of the polymer
35 tends to cause an undesirable increase in viscosity, leading

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to a need for more volatile solvent in the coating composition to give a viscosity suitable for application, for example by spraying. Too high a level of intermolecular crosslinking may cause gelation of the polymer solution or precipitation of crosslinked polymer. We have found that viscosity increase and gelation or precipitation are less liable to occur when the acid-functional polymer is a star polymer. It is believed that, in star polymers, any crosslinking has an increased tendency to be intramolecular between acid groups on different limbs of the same polymer molecule and this restricts formation of the type of intermolecular crosslinked network which causes viscosity increase and gelation or precipitation.

An alternative form of protected carboxylic acid functionality comprises carboxylic acid groups blocked by a monoamine or quaternary ammonium group, which preferably forms an organic solvent-soluble salt of the acid-functional polymer, for example as described in US-A-5,116,407.

The binder polymers containing carboxylic acid-functional polymers blocked by monoamine or quaternary ammonium groups are preferably prepared by reacting a star polymer having acid functionality, prepared as described above, with a monoamine or quaternary ammonium hydroxide to form the amine or quaternary ammonium salt. Alternatively, these binder polymers can be prepared by forming an amine salt or quaternary ammonium salt of an unsaturated carboxylic acid and polymerising the salt with at least one ethylenically unsaturated comonomer.

A further alternative form of protected carboxylic acid functionality comprises acid groups blocked by triorganosilyl groups which form hydrolysable silyl ester bonds with the carboxylic acid groups. Examples of triorganosilyl groups are trimethylsilyl, tributylsilyl, triisopropylsilyl, dimethylphenylsilyl and dimethylhexylsilyl. The binder star polymer can for example be

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produced by copolymerising a triorganosilyl ester of an unsaturated carboxylic acid such as acrylic, methacrylic or maleic acid with at least one ethylenically unsaturated comonomer in the presence of a free radical initiator and a
5 polyfunctional mercaptan. Examples of triorganosilyl esters are trimethylsilyl methacrylate, dimethylphenylsilyl methacrylate and triisopropylsilyl isoamyl maleate.

Further alternative forms of protected carboxylic acid functionality comprise acid groups blocked by quinolinyl
10 ester groups as described in US-A-4,426,464 or triarylmethyl ester groups as described in US-A-4,752,629. In both these cases the binder star polymer is preferably formed by copolymerisation of an ester of an unsaturated carboxylic acid with at least one ethylenically unsaturated comonomer
15 in the presence of a free radical initiator and a polyfunctional mercaptan.

A further alternative form of protected carboxylic acid functionality comprises triorganotin salt groups as used in presently available 'self-polishing' tin copolymer
20 antifouling paints. The triorganotin groups form hydrolysable tin ester bonds with the carboxylic acid groups. A triorganotin salt of an unsaturated carboxylic acid can be copolymerised with at least one ethylenically unsaturated comonomer in the presence of a free radical
25 initiator and a polyfunctional mercaptan. Examples of triorganotin salts are tributyltin methacrylate and triphenyltin acrylate and methacrylate. An antifouling coating having as binder a star polymer with triorganotin carboxylic functionality, for example a tributyltin
30 methacrylate/methyl methacrylate copolymer, can be formulated to have similar properties to commercial tin copolymer antifouling but with a lower volatile organic solvent content to achieve the same wet paint viscosity.

A binder polymer having protected sulphonic acid
35 functionality preferably comprises sulphonic acid groups

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blocked by a monoamine or quaternary ammonium group, which preferably forms a solvent-soluble salt of the acid-functional polymer.

The monoamine which is used to form the amine salt of the acid-functional polymer, for example the carboxylic or sulphonic acid-functional polymer, preferably contains a total of at least 6 carbon atoms, most preferably at least 10 carbon atoms, and it may contain up to 40 or more carbon atoms. The monoamine is preferably a tertiary amine, although primary or secondary amines can be used, as can quaternary ammonium groups. Examples of suitable tertiary amines are tributylamine, trihexylamine, tris(2-ethylhexyl) amine, tripropylamine, dimethyl dodecyl amine, dimethyl benzyl amine, dimethyl hexadecyl amine, di(dodecyl) methyl amine, dimethyl oleyl amine, dimethyl abietyl amine, dioctyl methyl amine and amines containing a mixture of aliphatic groups derived from a natural fat or oil such as dimethyl hydrogenated tallow amine, methyl di(hydrogenated tallow) amine, dimethyl coco amine, or methyl dicoco amine. Tertiary amines containing one long-chain aliphatic radical having 8 or more carbon atoms together with two lower alkyl groups such as methyl, for example dimethyl dodecyl amine, dimethyl oleyl amine, dimethyl abietyl amine or dimethyl coco amine, generally have biocidal properties against marine organisms such as algae and barnacles and may be preferred for use as the only ingredient having aquatic biocidal properties or to augment other biocides present in the antifouling coating. Tertiary or secondary amines containing at least two long-chain radicals such as dioctyl amine, dioctyl methyl amine, di(hydrogenated tallow) amine or methyl di(hydrogenated tallow) amine, and tertiary amines containing three alkyl groups of the same or similar chain length such as tributylamine, may be preferred in an antifouling coating containing known and registered biocides which are believed to give sufficient fouling prevention. Examples of suitable primary amines are diterpene-derived amines, for example Rosin Amine D, and aliphatic amines

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containing an organic group of 12 to 20 carbon atoms, for example a straight-chain alkyl or alkenyl amine such as dodecyl amine, hexadecyl amine, octadecyl amine or oleyl amine or mixtures of amines derived from aliphatic groups present in natural fats and oils such as tallow amine or hydrogenated tallow amine or coconut amine. Corresponding secondary and tertiary amines in which one or both of the amine hydrogens are replaced by methyl groups are also useful. Such primary and secondary amines generally have biocidal properties against marine organisms. Alternative amines which can be used to provide the blocking group are aralkylamines such as those sold commercially as "phenalkamines". Quaternary ammonium groups preferably contain a total of at least 8 carbon atoms, for example tetrabutyl ammonium, trimethyl benzyl ammonium, dodecyl trimethyl ammonium, hexadecyl trimethyl ammonium, oleyl trimethyl ammonium, benzyl dodecyl dimethyl ammonium, trioctyl methyl ammonium, dimethyl di(hydrogenated tallow) ammonium and trimethyl coconut ammonium.

20 The preferred process for preparing a binder polymer having protected sulphonic acid groups may depend on the relative convenience of polymerising a monomer having free sulphonic acid functionality or a monomer having protected sulphonic acid functionality. One preferred sulphonic acid monomer is AMPS. However, this is insoluble in common organic solvents so that, in preparing a binder polymer having protected sulphonic acid groups which are AMPS amine salt units, the AMPS amine salt is preferably prepared as a monomer and copolymerised with at least one ethylenically unsaturated monomer in organic solvent solution in the presence of a free radical initiator and a polyfunctional mercaptan.

A preferred method for preparing a binder polymer whose protected sulphonic acid groups are AMPS quaternary ammonium salt units is to copolymerise the methyl ester of AMPS with at least one ethylenically unsaturated monomer in the

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presence of a free radical initiator and a polyfunctional mercaptan to produce a star polymer containing AMPS methyl ester units. This can be reacted with a tertiary amine in approximately stoichiometric amounts at room temperature or
5 above to convert the AMPS methyl ester units to AMPS quaternary ammonium salt units; the methyl sulphonate ester group acts as an alkylating agent. Alternatively, the sulphonic acid monomer can be converted to amine salt or quaternary ammonium salt form before copolymerisation in the
10 presence of a polyfunctional mercaptan to produce a star polymer.

When the protected sulphonic acid groups are amine or quaternary ammonium salts of units of a sulphonated acrylic ester such as 2-sulphoethyl methacrylate or 2- or 3-
15 sulphopropyl methacrylate, the binder polymer is preferably produced by polymerising the sulphonic acid monomer to produce an acid-functional star polymer and then forming amine salt or quaternary ammonium salt groups by reaction with the amine or quaternary ammonium hydroxide.

20 When the protected sulphonic acid groups are amine or quaternary ammonium salts of an aromatic sulphonic acid such as styrene sulphonic acid, it may be most convenient to first copolymerise styrene sulphonyl chloride with at least one ethylenically unsaturated comonomer in the presence of
25 a free radical initiator and a polyfunctional mercaptan to produce a star polymer containing sulphonyl chloride groups. This can be reacted with a quaternary ammonium hydroxide or an amine in the presence of moisture to produce the binder polymer containing styrene sulphonic acid units in
30 quaternary ammonium salt or amine salt form.

Alternatively, a monomeric amine or quaternary ammonium salt of an aromatic sulphonic acid can be produced by reacting a sodium salt of the aromatic sulphonic acid with hydrogen chloride and an amine or quaternary ammonium
35 hydroxide. The monomeric amine or quaternary ammonium salt

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can then be polymerised with one or more ethylenically unsaturated comonomers in the presence of a polyfunctional mercaptan to produce the star binder polymer.

In general, using the polymerisation procedures described
5 above, star binder polymers can be prepared in organic solvent solution at concentrations of at least 50% by weight, usually 55-60% by weight. When such polymer solutions are blended with pigment to form a paint, the paint generally has a solids content of about 55% by volume
10 or even higher (45% or less volatile organic content) at a suitable viscosity for spray application, for example by airless spray, compared to a solids content of 40-50% by volume for most commercially available antifouling paints based on a water-erodible binder.

15 If a water-based paint is required, the star polymer can be prepared in organic solvent solution and dispersed in water, usually with the aid of a surfactant. The organic solvent can be partly or substantially completely removed from the resulting dispersion. For example, the star binder
20 polymer can be prepared in a solvent which is more volatile than water or forms an azeotrope with water and the solvent can be removed by distillation.

In an alternative way of preparing a water-based star binder polymer dispersion, the polymers can be prepared by
25 emulsion polymerisation. An ethylenically unsaturated monomer having protected acid functionality can be copolymerised with at least one ethylenically unsaturated comonomer as an oil-in-water emulsion using an anionic, cationic, nonionic or amphoteric surfactant in the presence
30 of a free radical initiator and a polyfunctional mercaptan.

The solution, dispersion or emulsion of the star polymer binder can be used as a clear antifouling varnish if the binder polymer has sufficient marine biocidal properties. A triorganotin acrylate or methacrylate star copolymer can

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for example be used without added biocide, as can a carboxylic acid-functional or sulphonic acid-functional star polymer in which the acid groups are blocked by a biocidal amine. More usually, the star polymer binder is blended 5 with a biocide for marine organisms and usually with a pigment using conventional paint-blending techniques. The biocide may itself be all or part of the pigment of the paint. If it is pigmented, the coating composition produced preferably has a pigment volume concentration of, for 10 example, 15 to 55%. The pigment is preferably a sparingly soluble pigment having a solubility in seawater of from 0.5 to 50 parts per million by weight and is most preferably a copper or zinc compound, for example cuprous oxide, cuprous thiocyanate, cuprous sulphate, zinc ethylene 15 bis(dithiocarbamate), zinc oxide, zinc dimethyl dithiocarbamate, zinc pyrithione, copper pyrithione, zinc diethyl dithiocarbamate, copper resinate or cuprous ethylene bis-(dithiocarbamate). These sparingly soluble pigments which are copper and zinc compounds are generally aquatic 20 biocides. Certain other sparingly soluble metalliferous pigments are biocides, for example manganese ethylene bis(dithiocarbamate). Copper metal can be used as a biocide, for example in flake or powder form.

The sparingly soluble metalliferous pigments produce 25 water-soluble metal compounds on reaction with seawater so that the pigment particles do not survive at the paint surface. This promotes the "self-polishing" action of the paint in which a leaving group is gradually hydrolysed from the acid-functional polymer and the resulting polymer 30 containing free acid groups gradually dissolves in seawater. Mixtures of sparingly soluble pigments can be used, for example cuprous oxide, cuprous thiocyanate or zinc ethylene bis (dithiocarbamate), which are highly effective biocidal pigments, can be mixed with zinc oxide, which is not 35 effective as a biocide but dissolves slightly more rapidly in seawater.

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The antifouling coating composition can contain a non-metalliferous biocide for marine organisms, for example tetramethyl thiuram disulphide, methylene bis(thiocyanate), captan, a substituted isothiazolone such as 4,5-dichloro-2-
5 N-octyl-4-isothiazolin-3-one, 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, N-3,4-dichlorophenyl-N', N'-dimethyl-urea, 2-(thiocyanomethylthio) benzothiazole, 2,4,5,6-tetrachloroisophthalonitrile or 2,3,5,6-tetrachloro-4-(methylsulphonyl) pyridine. Such a non-metalliferous
10 biocide can be used in addition to a sparingly soluble copper or zinc compound or one or more non-metalliferous biocides can be used as the only biocide of the coating in a copper-free, or even metal-free or pigment-free, antifouling coating. Many of these non-metalliferous
15 biocides are solid and all are sparingly soluble in seawater and may help the "self-polishing" action of the paint.

The antifouling coating composition can contain a minor amount of a co-film-former such as a polymer, resin or waxy material. The co-film-former may be chosen to modify the
20 hydrophilic or hydrophobic nature of the antifouling coating. For example, poly(vinyl alkyl ether)s are generally hydrophilic and tend to increase the hydrophilicity of the paint and thereby increase the rate of "self-polishing" of the paint. Vinyl alkyl ether/vinyl chloride copolymers are
25 generally less hydrophilic. Chlorinated paraffin waxes are generally hydrophobic and tend to retard the rate of "self-polishing" of the paint. The amount of such a co-film-former used is generally less than 40%, and preferably less than 20%, by weight based on the water-erodible star polymer
30 binder.

The coating composition can additionally contain a pigment which is not reactive with seawater and may be highly insoluble in seawater (solubility below 0.5 parts per million by weight) such as titanium dioxide or ferric oxide
35 or an organic pigment such as phthalocyanine pigment. Such highly insoluble pigments are preferably used at less than

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60% by weight of the total pigment component of the paint, most preferably less than 40% by weight.

The invention is illustrated by the following Examples:-

Example 1

5 1a Preparation of carboxylic acid-functional star polymer

In a 1L reaction vessel equipped with a thermometer, stirrer, condenser, nitrogen gas inlet and monomer feed inlet, xylene (225.0g) and butanol (225.0g) were heated to 80°C with stirring under an atmosphere of dry nitrogen gas.
10 To this mixture were added concurrently over 3 hours by means of peristaltic pumps a solution of methacrylic acid (67.17g), methyl methacrylate (196.89g), azo-bis-(isobutyronitrile) (AIBN, 22.6g) in xylene (109.2g) and butanol (109.2g), and a solution of a tetra-thiol-functional
15 chain-transfer agent, pentaerythritol tetramercapto-propionate (13.6g, equivalent to 1 mole % of total monomer charge) in xylene (33.7g) and butanol (33.7g). The temperature of the reaction mixture was maintained at 80°C throughout the addition period and for a further 1 hour.
20 Thereafter the mixture was heated to 95°C for 45 minutes, cooled and decanted to give a clear colourless solution of a poly(methacrylic acid)-co-(methyl methacrylate) star copolymer.

The star copolymer solution had 40% weight solids
25 (nominal), a viscosity of 400 mPa s (4 poise) at 25°C, and an acid value of 55mgKOH/g solution (theory 58mgKOH/g solution). Molecular weight determination by gel permeation chromatography (GPC) indicated Mn 3200 and Mw 5300 relative to polystyrene standards.

30 1b Preparation of carboxylic acid - amine salt-functional star polymer

To the acid-functional star copolymer solution described above in Example 1a (409.7g) was added hydrogenated ditallow

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methylamine (Armeen M2HT (Trade Mark), amine equivalent weight 523)(209.2g) to give a clear straw-coloured solution of the corresponding carboxylic acid-amine salt-functional star copolymer.

- 5 The acid-amine salt star copolymer solution had 60.3% weight solids (nominal) and viscosity 400 mPa s (4 poise) at 25°C.

1c Antifouling Paint Preparation

The following materials were mixed in a high-speed
10 disperser to form an antifouling paint from the polymer prepared in Example 1b.

	Component	% by weight
	Polymer solution, Example 1b	17.49
	Cuprous oxide	67.93
15	"Lutonal A25" vinyl ether polymer	1.48
	Fumed silica	2.50
	Xylene	10.60

The resulting paint had pigment volume concentration (PVC) 50% and Volume solids 55%.

20

Example 2

2a Preparation of sulphonic acid-functional star polymer

The general procedure outlined above in Example 1a was modified such that a triple feed process was used. Thus, to an initial pot-charge of butanol (100.0g) were added
25 concurrently a solution of n-butyl methacrylate (259.6g) and AIBN (17.6g) in butanol (120.0g), a solution of 2-sulphoethyl methacrylate (62.5g) in butanol (39.3g) and a solution of pentaerythritol tetramercaptopropionate (10.5g, equivalent to 1 mole % of total monomer charge) in xylene
30 (91.4g). After processing, the resulting clear, golden solution of (2-sulphoethyl methacrylate)-co-(n-butyl methacrylate) star copolymer had 50% weight solids

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(nominal), a viscosity of 100 mPa s (1 poise) at 25°C, and an acid value of 23.9mgKOH/g solution (theory 25.8mgKOH/g solution). Molecular weight determination by GPC indicated Mn 1400 and Mw 3700 relative to polystyrene standards.

5 2b Preparation of sulphonic acid - amine salt-functional star polymer

To the sulphonic acid-functional star copolymer solution described above in Example 2a (500.0g) was added hydrogenated ditallowmethylaniline (Armeen M2HT) (111.6g) to
10 give a clear, pale yellow solution of the corresponding sulphonic acid - amine salt-functional star copolymer.

The sulphonic acid - amine star copolymer solution had 59.0% weight solids (nominal) and viscosity 100 mPa s (1 poise) at 25°C.

15 2c Antifouling Paint Preparation

The following materials were mixed in a high-speed disperser to form an antifouling paint from the polymer prepared in Example 2b:-

	Component	% by weight
20	Polymer Solution, Example 2b	19.40
	Cuprous oxide	67.78
	"Lutonal A25"	1.48
	Fumed Silica	2.50
	Xylene	8.83

25 The resulting paint had PVC 50% and Volume solids 55%.

Example 3

3a Preparation of a (tributyltin methacrylate)-co-(methyl methacrylate) star copolymer

Following the procedure detailed in Example 1a, to an
30 initial pot-charge of xylene (137.3g) were added

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concurrently a solution of tributyltin methacrylate (208.8g), methyl methacrylate (140.1g) and AIBN (16.1g) in xylene (181.8g) and a solution of pentaerythritol tetramercaptopropionate (9.6g, equivalent to 1 mole % of 5 total monomer charge) in xylene (56g).

After processing, the resulting clear, colourless solution of (tributyltin methacrylate)-co-(methyl methacrylate) star copolymer had 50% weight solids (nominal), a viscosity of 100 mPa s (1 poise) at 25°C, and 10 an acid value of 40 mgKOH/g solution (theory 41 mgKOH/g solution). Molecular weight determination by GPC indicated Mn 4200 and Mw 9700 relative to polystyrene standards.

3b Antifouling Paint Preparation

The following materials were mixed in a high-speed 15 disperser to form an antifouling paint from the polymer prepared in Example 3a.

	Component	% by weight
	Polymer solution of Example 3a	32.43
	Cuprous oxide	63.57
20	"Lutonal A25"	1.40
	Fumed silica	2.50
	Xylene	0.10

The resulting paint had PVC 50% and Volume solids 55%.

Example 4

25 4a Preparation of carboxylic acid-functional star polymer

Following the procedure detailed in Example 1a, to an initial pot-charge of xylene (191.7g) and butanol (38.3g) were added concurrently a solution of acrylic acid (113.0g), ethyl acrylate (563.0g) and AIBN (58.9g) in xylene (254.6g) 30 and butanol (50.9g) and a solution of pentaerythritol tetramercaptopropionate (35.1g, equivalent to 1 mole % of total monomer charge) in xylene (78.7g) and butanol (15.8g).

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After processing, the resulting clear, colourless solution of (acrylic acid)-co-(ethyl acrylate) star copolymer had 55% weight solids (nominal), a viscosity of 100 mPa s (1 poise) at 25°C and an acid value of 56mgKOH/g solution (theory 65mgKOH/g solution). Molecular weight determination by GPC indicated Mn 3300 and Mw 6700 relative to polystyrene standards.

4b Preparation of poly-Carboxylic acid-naphthenic acid - copper complex

Following the general procedure of Example 1 of EP-A-342,276, a mixture of the acrylic acid star copolymer described above in Example 4a (650.0g), naphthenic acid (acid value 200 mgKOH/g)(181.3g), copper acetate monohydrate (129.0g) and xylene (118.5g) was heated to 145°C over 6 hours with removal of volatiles by means of a distillation head until the acid value of the mixture was 148mgKOH/g polymer expressed as 100% non-volatiles. Throughout the reaction period the volume of reagents in the reaction vessel was maintained at constant volume by the addition of xylene to replace the volatiles lost by distillation. At the end of the reaction, butanol (132.4g) was added to give a dark green solution of the star copolymeric carboxylic acid - naphthenic acid - copper complex having 45% weight solids and viscosity 100 mPa s (1 poise) at 25°C.

4c Antifouling Paint Preparation

The following materials were mixed in a high-speed disperser to form an antifouling paint from the polymer prepared in Example 4b:-

	Component	% by weight
30	Polymer solution of Example 4b	29.16
	Cuprous oxide	66.06
	"Lutonal A25"	1.45
	Fumed silica	2.50
	Xylene	0.84

The resulting paint had PVC 50% and Volume solids 55%.

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Example 55a Preparation of poly-carboxylic acid - neo-tridecanoic acid - copper complex

Following the procedure of Example 4b a mixture of the 5 acrylic acid star copolymer described above in Example 4a (575.0g), neo-tridecanoic acid (120.6g), copper acetate monohydrate (144.1g) and xylene (185.8g) was heated to 145°C over 6 hours with removal of volatiles by means of a distillation head until the acid value of the mixture was 10 160 mgKOH/g polymer expressed at 100% non-volatiles. Throughout the reaction period the volume of reagents in the reaction vessel was maintained at constant volume by the addition of xylene to replace the volatiles lost by distillation. At the end of the reaction, butanol (115.0g) 15 was added to give a dark green solution of the star copolymeric carboxylic acid - neo-tridecanoic acid - copper complex having 45% weight solids and viscosity 100 mPa s (1 poise) at 25°C.

5b Antifouling Paint Preparation

20 The following materials were mixed in a high-speed disperser to form an antifouling paint from the polymer proposed in Example 5a:

	Component	% by weight
	Polymer solution of Example 5a	29.17
25	Cuprous oxide	66.00
	"Lutonal A25"	1.44
	Fumed silica	2.50
	Xylene	0.89

The resulting paint had PVC 50% and Volume solids 55%.

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CLAIMS

1. An antifouling coating composition comprising a water-erodible binder polymer having protected acid functionality and including an ingredient having biocidal properties for aquatic fouling organisms, characterised in that the binder polymer is a polymer having at least 3 limbs radiating from a central core, the acid functionality being present in the said limbs of the polymer.
2. An antifouling coating composition according to claim 1, characterised in that the acid functionality is carboxylic acid functionality.
3. An antifouling coating composition according to claim 1 or claim 2, characterised in that the acid functionality is protected by a divalent metal or organometallic radical bonded to the residue of a monobasic organic acid.
4. An antifouling coating composition according to claim 3, characterised in that said divalent metal is copper and said monobasic organic acid is a carboxylic acid.
5. An antifouling coating composition according to claim 2, characterised in that the protected acid functionality comprises carboxylic acid groups blocked by a monoamine or quaternary ammonium group.
6. An antifouling coating composition according to claim 2, characterised in that the protected acid functionality comprises carboxylic acid groups blocked by triorganosilyl groups which form hydrolysable silyl ester bonds with the carboxylic acid groups.
7. An antifouling coating composition according to claim 2, characterised in that the protected acid functionality comprises carboxylic acid groups blocked by triorganotin groups which form hydrolysable tin ester bonds with the

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with the carboxylic acid groups.

8. An antifouling coating composition according to claim 1, characterised in that the acid functionality is sulphonic acid functionality.

5 9. An antifouling coating composition according to claim 8, characterised in that the protected acid functionality comprises sulphonic acid groups blocked by a monoamine or quaternary ammonium group.

10 10. An antifouling coating composition according to any 10 of claims 1 to 9, characterised in that the binder polymer is a star polymer having 3 to 8 limbs.

11. An antifouling coating composition according to any of claims 1 to 10, characterised in that the binder polymer has a weight average molecular weight of 3000 to 50,000 as 15 measured by gel permeation chromatography against a polystyrene standard.

12. An antifouling coating composition according to any of claims 1 to 11, characterised in that the weight average molecular weight of each limb of the binder polymer is in 20 the range 1000 to 6000.

13. An antifouling coating composition according to any of claims 1 to 12, characterised in that the binder polymer has an average functionality of at least one protected acid group per limb of the polymer.

25 14. An antifouling coating composition according to any of claims 1 to 13, characterised in that the central core of the binder polymer is the residue of a polyfunctional mercaptan having 3 to 8 -SH groups.

15. An antifouling coating composition according to any 30 of claims 1 to 14, characterised in that the composition

contains at least 55% by volume non-volatile material and has a viscosity suitable for application by conventional airless spray.

16. A process for the preparation of a binder polymer 5 having protected acid functionality, characterised in that an ethylenically unsaturated monomer having acid functionality and at least one ethylenically unsaturated comonomer are copolymerised by addition polymerisation in the presence of a polyfunctional mercaptan having 3 to 8 -SH 10 groups to form a star polymer having acid functionality, and the star polymer having acid functionality is reacted with a reagent introducing blocking groups which protect the acid functionality.

17. A process according to claim 16, characterised in 15 that the star polymer having acid functionality is reacted with:

- (a) a salt of a low-boiling organic monobasic acid and a divalent metal, and
- (b) a high-boiling organic monobasic acid

20 at an elevated temperature while removing from the reaction the low-boiling organic monobasic acid which is evolved.

18. A process for the preparation of a binder polymer having protected acid functionality, characterised in that an ethylenically unsaturated monomer having protected acid 25 functionality and at least one ethylenically unsaturated comonomer are copolymerised by addition polymerisation in the presence of a polyfunctional mercaptan having 3 to 8 -SH groups to form a star polymer having protected acid functionality.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GP 95/01758

A. CLASSIFICATION OF SUBJECT MATTER

C 09 D 5/16

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 09 D, C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A, 0 448 224 (IMPERIAL CHEMICAL INDUSTRIES PLC) 25 September 1991 (25.09.91), claims; page 2, lines 1-6; page 3, lines 38-43 (cited in the application). --	1, 2, 10-16, 18
X	US, A, 4 659 783 (SPINELLI) 21 April 1987 (21.04.87), claims; examples. ----	1, 2, 10-13

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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Date of the actual completion of the international search

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ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/GB 95/01758 SAE 114861

In diesem Anhang sind die Mitglieder
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Im Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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